

# Alpha Furildioxime As a Reagent For the Detection and Determination of Nickel

**THE DETERMINATION OF NICKEL IN STEEL  
BY MEANS OF ALPHA FURILDIOXIME**

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## A Dissertation

Submitted in Partial Fulfillment of the Requirements for the Degree  
of Doctor of Science in the University of Michigan.

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By  
BYRON A. SOULE

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Byron A. Soule.

Ann Arbor, Michigan.  
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**Introduction**

The change in status of furfural from a laboratory curiosity to a commercial product has made it seem worth while to investigate the properties of its derivative, alpha furildioxime, as a reagent for the detection and determination of nickel, especially in steel. Although Tschugaeff (1) mentioned twelve, hitherto only two members of the dioxime series have been studied from the standpoint of their use in chemical analysis. Brunck (2) recommended alpha dimethylglyoxime in 1907 and Attack (3) suggested alpha benzildioxime in 1913. Neither of these reagents has come into very general use in the industrial field as indicated by F. C. Phillips' book (4) "Methods of Iron Analysis" in which are given the methods of some fourteen laboratories of the Pittsburgh, Pennsylvania, district. Eight laboratories separate nickel from iron by ether extraction while three others use the basic acetate method. All except one precipitate nickel as the sulfide and ignite to the oxide.

In spite of the fact that the dioxime methods are much faster and more accurate, the reasons for this state of affairs are perhaps not difficult to find. Alpha dimethylglyoxime is expensive and soluble only in organic media; alpha benzildioxime while probably the most easily prepared of the alpha dioximes is so insoluble that it tends to crystallize out and contaminate the precipitate. This objection might be overcome by introducing the proper substituent into the benzene ring; but up to the present time nothing has been found in the literature to indicate that the idea has been tried.

Thus it was with the hope of finding a cheaper, water-soluble alpha dioxime that the properties of alpha furildioxime were investigated.

### Historical Review

The development of analytical procedure for nickel falls naturally into three periods; the one method stage, the many methods stage and the present stage which might be characterized as the three methods stage.

(a) The one method stage. (1751 to 1860).

Ores containing nickel were encountered as far back as 1694 (5), especially niccolite, which was called "Kupfernickel" (meaning devil copper) by the miners of Saxony because of its red color and failure to yield copper upon smelting. In 1726 J. H. Link (6) wrote that this same mineral was a cobalt ore mixed with copper, as one could see by the green color of the nitrate. Rather fantastic was the belief of many people that kupfernickel was burnt cobalt that had lost its soul. (7) The mystery was solved however by the Swedish chemist Cronstedt (8) who, between 1751 and 1754 isolated and named the element nickel, which when combined with arsenic forms the red niccolite ( $\text{Ni As}$ ) called kupfernickel.

The major portion of the century following Cronstedt's work was spent considering the question,—Is nickel an element, a compound, or a mixture? Thus when Gauhe (9) in 1865 wrote his critical study "Ueber die Bestimmungsformen des Kobalts und Nickels" he found only three methods worth mentioning. The first was precipitation as  $\text{Ni(OH)}_2$  by means of caustic potash followed by ignition to  $\text{NiO}$ ; the second, precipitation and weighing as  $\text{NiSO}_4$ ; and the third, precipitation and weighing as  $\text{NiS}$  or  $\text{Ni}_2\text{S}$ . He indicated that the first method was the best and most commonly used. Later work (10) has shown that the oxide method even with its subsequent improvements (11) (12) (13) gives results in error by as much as five per cent, due to contamination of the precipitate by alkali and silica and reduction of the oxide to metallic nickel during ignition. Gauhe, in using the second method, found it difficult to determine when ignition was complete, whereas he found the third, either in its original form or as modified by H. Rose, practically useless, because the nickel sulfide when ready for weighing was contaminated with nickel oxide and nickel sulfate due to changes during ignition.

(b) The many methods stage. (1860 to 1905).

With the increase in commercial importance of nickel there came a demand for more accurate methods of analysis. This was met through work along three lines; (1) development of gravimetric methods, (2) development of volumetric methods, (3) rise of electrolytic methods.

### (1) Gravimetric Methods.

Naturally the first attempts were toward improvement of the oxide method with the trend strongly in favor of precipitation as nickelic hydroxide followed by ignition to the trioxide, chiefly because it afforded a means of separation from cobalt. A wide variety of reagents and modifications of procedure was proposed. None of them has withstood the test of time. (14)

As regards improvement of the sulfide method, serious difficulties were encountered in the quantitative precipitation of nickel sulfide, and in addition no simple procedure was found for obtaining NiS in a weighable condition, i. e., uncontaminated with NiO or NiSO<sub>4</sub>. (15) (16).

The sulfate method (17) involving precipitation and weighing as NiSO<sub>4</sub> advocated during this period was found to be of little value because it was difficult to drive off all sulfuric acid and at the same time avoid conversion of some of the sulfate to nickel oxide.

The oxalate method with its many modifications (18) (19) was found to be of very limited use because in the presence of alkali or ammonium salts the soluble double oxalate, M<sub>2</sub>Ni(C<sub>2</sub>O<sub>4</sub>)<sub>2</sub>, was formed. (20) It was also discovered that nickel was incompletely precipitated as the oxalate. (21)

The only other gravimetric method of the period was that involving precipitation as the phosphate, first mentioned by Thomas Moore (22) and later recommended by Clark (23). The method was found satisfactory for the determination but not for the separation of nickel.

### (2) Volumetric Methods.

Although a large number of volumetric methods for nickel have been advocated, only one has proved to be very useful. It involves the use of potassium cyanide and is based upon the reaction:—



When first suggested by Thomas Moore in 1889 (24) the best indicator he had found was cupric ferrocyanide. This was a serious handicap but was overcome six years later by Campbell and Andrews. (25) They advised the use of an opalescence of silver iodide for determining the end-point of titration. (26) In this modified form the method has endured. Slight variations have been recommended at different times but they have not been of fundamental importance. (27) (28)



### (3) Rise of Electrolytic Methods.

Gibbs first suggested the determination of nickel electrolytically. (29) He deposited the metal on a platinum cathode from an ammoniacal solution of nickel sulfate. A few years later Fresenius and Bergman (30) studied the method and found it excellent. Then other investigators began to suggest all sorts of changes. Fischer (31) expressed a preference for the complex compounds while Classen introduced oxalates, especially ammonium oxalate, into the electrolytic bath. (32) Phosphate (33) and borates (34) were claimed to have beneficial effects, etc. However, the oldest method is still in use with perhaps one difference, namely the rate of deposition. In the earlier days it was deemed necessary to deposit metals very slowly to insure good results, five to twelve hours were taken for a sample that nowadays would be finished in less than one hour. (35)

Summarizing the work of the second period we see that only two methods for the determination of nickel were developed, the electrolytic and the cyanide titration. Both were found to be simple, accurate, dependable and capable of fairly wide application, especially the latter method which could be used in the presence of iron, zinc, chromium, tungsten, manganese, etc. There remained, however, one gap to be filled; a good gravimetric method was much desired. It was supplied early in the third period.

#### (c) The present stage. (1905 to 1924)

In 1905 while preparing inorganic salts of various oximes Tschugaeff (36) noted that "the alpha dioximes differ in behavior from all other oximes to the extent that they form very stable and to all appearances complex compounds with many of the heavy metals of the eighth group of the Periodic System, especially nickel, cobalt, iron, platinum, palladium, and copper." Further experimentation led him to recommend one of the alpha dioximes, previously named dimethylglyoxime, (37) as a specific reagent for the detection of nickel. (38) Apparently not interested in the quantitative aspects of the case Tschugaeff returned to his study of the behavior of other dioximes. Thus Brunck (39) in 1907 had a clear field when he recommended alpha dimethylglyoxime for the separation and determination of nickel. He had discovered an excellent method and incidentally had written an important chapter in the story of the application of organic reagents to the analysis of inorganic substances.

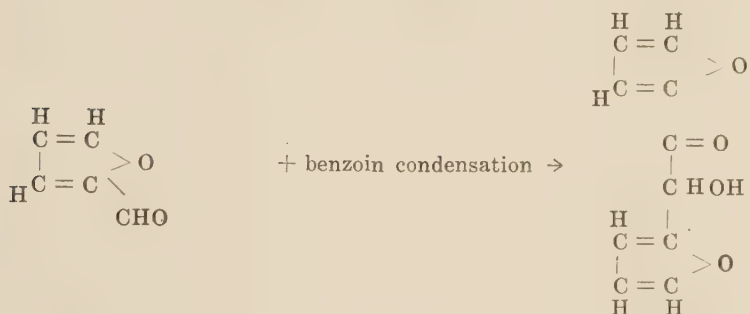
Three other organic reagents have at different times been suggested for the separation or determination of nickel; potassium xanthate, (40) dicyandiamidine (41) alpha benzildioxime (42) none of which has been a serious competitor of dimethylglyoxime.



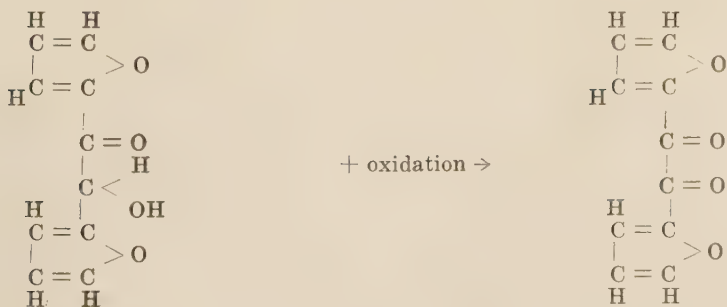
## Experimental Part

**Preparation of the reagent.**—The different steps in the preparation of alpha furildioxime were as follows:

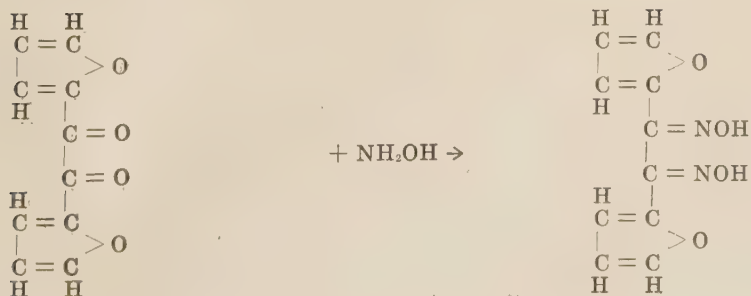
(a) Furfural condensed to furoin.



(b) Furoin oxidized to furil.



(c) Furil converted to alpha furildioxime.



Commercial furfural\* was used as the starting material. This furfural, by distillation under reduced pressure, was found to contain about 4.5% water as the chief impurity. Trial runs with samples of carefully redistilled and of commercial material revealed no noticeable difference in yield or quality of the product. Hence no preliminary purification was deemed necessary:

The method of synthesis for steps (a) and (b), was essentially that of Emil Fischer. (43) He obtained fair results, when preparing furoin, by refluxing, for thirty to forty minutes, a mixture corresponding to the following:—

|                          |      |       |
|--------------------------|------|-------|
| Furfural .....           | 1    | Mole  |
| Alcohol, Ethyl .....     | 1.5  | Moles |
| Water .....              | 10.7 | Moles |
| Pot. Cyanide (95%) ..... | 0.14 | Mole  |

After cooling, filtering, washing, and purifying, he secured a yield of about twenty-five per cent.

At first attempts were made by Soule to improve this yield. The only results were a slight modification of the ingredients and a change in the proportions used, thus:—

|                       |      |       |
|-----------------------|------|-------|
| Furfural .....        | 1.0  | Mole  |
| Alcohol, Methyl ..... | 1.5  | Moles |
| Water .....           | 6.0  | Moles |
| Sodium cyanide .....  | 0.12 | mole  |

This gave a product easy to handle which, after washing as directed by Fischer, was used for the next step without further purification.

The second operation, oxidation of the furoin to furil, was effected by bubbling air thru a solution of furoin in dilute alcohol containing just enough sodium hydroxide to prevent precipitation of the furoin at the temperature of reaction, 0°C, and, of course, to secure an alkaline medium. The yield was good though not quantitative, due probably to the use of an impure raw material.

The procedure for the final step was a modification of that recommended by Macnair. (44) All crude furil obtained, melting above 160°C, was changed into the alpha dioxime by refluxing for five to six hours with hydroxylamine hydrochloride in the presence of methyl alcohol. Yields of light brown crystals as high as eighty-five per cent were obtained. The crystals were purified by recrystallization from water (44) two or three times. Though contaminated with a small amount of furoinoxime(?) the product was found to be suitable for the major portion of the quantitative work here described. Quali-

\*The furfural used in this investigation was furnished by the Miner Laboratories, Chicago, Illinois.

tative tests and experiments in which the dioxime was weighed were made with material purified by recrystallization from alcohol. This gave colorless crystals which appeared to effloresce while drying, leaving a white powdery residue softening and decomposing at 168°C (uncorrected).

The dioxime crystals, when used for analytical purposes, were dissolved in hot water to give a two per cent solution, or in warm alcohol to give a ten or a fifteen per cent solution. On cooling some of the solute crystallized out; otherwise no change was noted in samples that were made up and left on the work bench for several months in glass stoppered bottles.

**Standard Nickel Solution:**—Qualitative and preliminary quantitative experiments were performed using a standardized solution prepared from Mond process nickel, containing small amounts of Fe and C as impurities.

The metal was dissolved in dilute nitric acid. After removal of the carbonaceous residue by filtration, sufficient ammonia water was added to redissolve all but a small amount of the nickel hydroxide first formed. This precipitate aided in the complete separation of ferric hydroxide. The ammonio-nickel nitrate was next converted into nickel sulfate. Samples of this were tested for iron and cobalt. The quantity of iron present was less than one part in one hundred thousand as indicated by the thiocyanate test. Cobalt could not be detected by Vogel's reaction. (45)

The standard solution was then prepared by dissolving an amount of the nickel sulfate equivalent to six grams of metal in six liters of water. (The water contained ten cubic centimeters of sulfuric acid (95%) added to prevent hydrolysis.) The liquid was stored in a bottle through the stopper of which passed a siphon tube, a thermometer and an air inlet. The inlet tube was connected to a suitable train of gas washing bottles.

After a few days samples of the solution were withdrawn and measured by means of a carefully calibrated burette. The amount of nickel in each sample was determined. (46) The mean of four electrolyses gave a value of 0.001087 gm. of nickel per cubic centimeter. The mean of four gravimetric determinations involving precipitation and weighing as nickel dimethylglyoxime (47) gave a slightly lower value, 0.001078 gm. of nickel per cubic centimeter.

Several months later, when approximately five liters of the solution had been used, check analyses were made by the electrolytic



method. The mean of four determinations was 0.001084 gm. of nickel per cubic centimeter, showing that the method of storage had been efficient and that the concentration of nickel in the solution had not changed during the time it was being used.

TABLE I  
Standardization of Nickel Solution.

(a) Electrolysis of freshly prepared solution.

| Soln. Taken | Ni found | Ni per c.c.          |
|-------------|----------|----------------------|
| c.c.        | gm       | gm                   |
| 49.83       | .0541    | .001085              |
| 49.83       | .0543    | .001089              |
| 45.20       | .0490    | .001084              |
| 47.72       | .0520    | .001089              |
|             |          | Average..... .001087 |

(b) Gravimetric method.

| Soln. Taken | Dioxime | Ni found | Ni per c.c.          |
|-------------|---------|----------|----------------------|
| c.c.        | gm      | gm       | gm                   |
| 30.05       | .1597   | .0324    | .001080              |
| 33.12       | .1762   | .0358    | .001081              |
| 35.16       | .1862   | .0378    | .001076              |
| 40.05       | .2123   | .0431    | .001077              |
|             |         |          | Average..... .001078 |

(c) Electrolysis after several months.

| Soln. Taken | Ni found | Ni per c.c.          |
|-------------|----------|----------------------|
| c.c.        | gm       | gm                   |
| 50.05       | .0541    | .001081              |
| 50.05       | .0542    | .001083              |
| 49.05       | .0534    | .001088              |
| 49.05       | .0533    | .001087              |
|             |          | Average..... .001084 |

(Note:—In this investigation the gravimetric factor was the one employed, due to procedure relationship.)

### Delicacy of the Test for Nickel.

The determination of the delicacy of a test involves two important factors in addition to the amount of substance detectable. That is of primary importance of course, but of almost equal rank are the volume of solution used and the time required for the test. Yet a search of the literature yields few statements of sensitivity accompanied by this information. In the case of dimethylglyoxime we have merely the declaration by Tschugaeff (48) that it will detect less than one part of nickel in 400,000. Attack, (49) when reporting on alpha benzildioxime, was more specific. He stated that "it was found

possible to detect immediately less than one part of nickel in 2,000,000 parts of water, using a volume of 5cc. corresponding to 0.002 mgrm. of nickel."

It has therefore been deemed advisable to give a somewhat detailed account of the procedure when determining the sensitivity of alpha furildioxime.

A solution of nickel sulfate was prepared such that twenty cubic centimeters contained one milligram of nickel. One-half of the liquid was removed by means of a calibrated pipette and diluted to twenty cubic centimeters. This also was divided into two equal parts, one of which was diluted. The process was thus repeated, reserving one-half each time, until ten samples were obtained, the quantity of nickel in the first being one-half milligram while each succeeding portion had just half as much as the one preceding. In other words, the first sample represented one part of nickel in 20,000; the second, one in 40,000; the third, one in 80,000 and so on down to one part in 10,240,000. Two more sets were prepared in the same way. Then to each of the thirty portions was added one drop of ammonia water. (ca. 28%). Next, to each of the first set was added a few drops of dimethylglyoxime; to each of the second ten, alpha benzildioxime; and to each of the last ten, alpha furildioxime. The results obtained immediately after addition of the reagents have been assembled in Table II,

TABLE II

A comparison of the sensitivity of the three dioximes  
under the same conditions.

|    | Ni present<br>mgm | One part<br>Ni in | Dimethyl-<br>glyoxime | alpha benzil<br>dioxime | alpha furil-<br>dioxime |
|----|-------------------|-------------------|-----------------------|-------------------------|-------------------------|
| 1  | 0.5               | 20,000            | ppt.                  | ppt.                    | ppt.                    |
| 2  | .25               | 40,000            | ppt.                  | ppt.                    | ppt.                    |
| 3  | .12               | 80,000            | ppt.                  | ppt.                    | ppt.                    |
| 4  | .06               | 160,000           | ppt.                  | ppt.                    | ppt.                    |
| 5  | .03               | 320,000           | ....                  | ppt.                    | ppt.                    |
| 6  | .015              | 640,000           | ....                  | ....                    | deep rose               |
| 7  | .0075             | 1,280,000         | ....                  | ....                    | orange color            |
| 8  | .0037             | 2,560,000         | ....                  | ....                    | pale orange<br>color    |
| 9  | .0018             | 5,120,000         | ....                  | ....                    | pale orange<br>color    |
| 10 | .0009             | 10,240,000        | ....                  | ....                    | same as blank           |

from which it will be seen that under the condition of the test dimethylglyoxime was found to be the least delicate. The other two gave no precipitate after the fifth tube, while alpha furildioxime gave a dis-

tinct color reaction down to the tenth. Of course the results do not represent the maximum sensitivity of the dioximes because no attempt was made to perform the tests under the most favorable conditions, but they do give at least a comparative idea.

Experiments were next made to determine the least amount of nickel that could be detected with certainty the test depending upon the formation of a precipitate. This was found to be one part in six million parts of solution. The method was as follows:—

To twenty-five cubic centimeters of the dilute nickel solution (1:6,000,000) in a test tube were added about two cubic centimeters of ammonia water, (1:4) then one-tenth of a cubic centimeter of a ten per cent alcoholic solution of alpha furildioxime. The tube was stoppered and shaken vigorously for thirty seconds, by the watch. Immediate filtration left a distinct red precipitate on the filter paper (50).

The concentration of ammonium hydroxide was found to be of importance in the above test, there being an upper and lower limit for maximum precipitation. Too little ammonia did not make the solution sufficiently alkaline, too much exercised a solvent effect. The range in one set of experiments was from 1.9 to 2.5 cubic centimeters the optimum being 2.2 cubic centimeters. The addition of two cubic centimeters of a ten per cent ammonium sulfate solution increased by one cubic centimeter the amount of ammonia water required.

After determining the sensitivity of the alpha furildioxime reaction, tests were made to see if alpha benzildioxime would give the same results under the same conditions. All tests were negative. Since dimethylglyoxime is less sensitive than alpha benzildioxime, no attempt was made to use it according to the method under discussion.

Assuming the value given by Tschugaeff and Atack to be correct, Table III gives a comparative summary of the sensitivity of the three dioximes.

TABLE III

| Reagent             | Ratio       | Sensitivity<br>mgm. per c.c. |
|---------------------|-------------|------------------------------|
| Dimethylglyoxime    | 1:400,000   | 0.0024                       |
| Alpha Benzildioxime | 1:2,000,000 | .0002                        |
| Alpha Furildioxime  | 1:6,000,000 | .00016                       |

A search of the literature has disclosed only one reagent possessing a greater sensitivity for nickel than alpha furildioxime. Potassium dithio-oxalate, according to Jones and Tasker (51), gives a magenta color easily visible in a test tube when one part of nickel is

present in eight million of solution. This however is a color test, not a precipitation reaction.

**The Use of Alpha Furildioxime in Chemical Microscopy.**—In spite of the fact that alpha furildioxime will detect a minute amount of nickel it has not been found entirely suitable as a reagent in chemical microscopy. This is because no simple process has yet been discovered which will result in the formation of a crystalline precipitate.

**The Use of Alpha Furildioxime in Qualitative Analysis.**—Qualitative tests were in general performed by adding a few drops of the reagent to a faintly ammoniacal solution of the substance to be tested. No precipitation or color change was observed in the case of ammonio-silver, copper, or zinc. Ammonio-cobaltous solution darkened in color. Results with manganese were negative. Ferric iron, chromium, or aluminum gave no visible action when tested in ammoniacal solutions containing citrate or tartrate. In fact, with one exception no ion was found, other than the nickelous, that would give a precipitate under the conditions specified. (Platinum and palladium have not been considered in this investigation). The exception was ferrous iron which in a solution containing less than one part in three million gave a greenish color. Upon increasing the concentration the color darkened through blue to purple with the final formation of a purple precipitate either flocculent or in the form of small dendritic crystals, depending upon the speed of separation. This did not obscure the qualitative test for nickel but gave rise to high results in quantitative work where it became an important source of error when the nickel furildioxime was to be weighed.

**Interferences.**—In addition to the interference mentioned above it was found that small amounts of nickel could not be detected in the presence of large amounts of ammonio-cobaltous ion. Oxidation of the cobalt (52) eliminated the difficulty. To avoid precipitation of manganic hydroxide when testing for nickel in a solution containing manganese it was found that Brunck's expedient (53) would work satisfactorily, viz., performing the test in the presence of acetic acid and sodium acetate. This modification also gave good results in the presence of cobalt and zinc.

It should be emphasized that purified alpha furildioxime was used for the qualitative tests. An impure sample gave tests with several



of the ions mentioned, particularly copper and cobalt. The precipitates appeared the same as those obtained when using furoinoxime in another investigation. (54) It is possible that this compound was the interfering impurity.

### The Use of Alpha Furildioxime in Quantitative Analysis.—

#### (a) Composition of the precipitate.—

The composition of nickel furildioxime was determined, in-so-far as the nickel content is concerned, by Chosinsky, who worked under the direction of Tschugaeff. (55) Details of the method were not given other than that the nickel was weighed as NiO. Chosinsky obtained results corresponding to 11.85% nickel for the formula  $C_{20}H_{14}N_4O_8Ni$  whereas the theoretical value is 11.81%. No specific attempt was made to check this figure since calculations involving data obtained in various experiments indicated that it was correct.

The nickel content of the related compounds, dimethylglyoxime and alpha benzildioxime, is given in Table IV.

TABLE IV

| Nickel Content of the Dioximes. |            |
|---------------------------------|------------|
| Reagent                         | Ni content |
| Dimethylglyoxime                | 20.32%     |
| Alpha Benzildioxime             | 10.93%     |
| Alpha Furildioxime              | 11.81%     |

It will be seen from this table that the quantity of nickel in the two ring compounds is about half what it is in the dimethyl derivative, and that there is a difference of less than one per cent between the value for alpha benzil- and that for alpha furildioxime, practically negligible as a basis for choice in analytical work.

#### (b) Preliminary Analyses.—

Preliminary experiments were made to determine the effect of the various reagents used in the determination of nickel. First, separation in the presence of ammonium salts was tried. This was followed by a study of the effect of the common compounds used to prevent the precipitation of iron. Some of the results obtained are given in Table V. It will be seen from these data that the compounds considered do not interfere.

TABLE V

Showing that alpha furildioxime will quantitatively separate nickel from solutions containing various compounds used in analysis.

(a) Ammonium salts.

| Salt added                   | Amount gm. | Ni taken gm. | Ni recov. gm. | Dif. mgm. |
|------------------------------|------------|--------------|---------------|-----------|
| $\text{NH}_4\text{Cl}$       | 2          | .0218        | .0218         | 0         |
| $\text{NH}_4\text{Cl}$       | 3          | .0218        | .0218         | 0         |
| $(\text{NH}_4)_2\text{SO}_4$ | 2          | .0225        | .0226         | +0.1      |
| $(\text{NH}_4)_2\text{SO}_4$ | 4          | .0217        | .0216         | -0.1      |
| $\text{NH}_4\text{NO}_3$     | 2          | .0217        | .0215         | -0.2      |

(b) Compounds used to prevent precipitation of ferric iron.

| Salt added                        | Amount gm. | Ni taken gm. | Ni recov. gm. | Dif. mgm. |
|-----------------------------------|------------|--------------|---------------|-----------|
| Citric acid                       | 2          | .0277        | .0279         | +0.2      |
| Na citrate                        | 2          | .0217        | .0218         | +0.1      |
| Tartaric acid                     | 2          | .0217        | .0216         | -0.1      |
| Na tartrate                       | 2          | .0217        | .0217         | 0         |
| $\text{Na}_4\text{P}_2\text{O}_7$ | 2          | .0218        | .0217         | -0.1      |

(c) Method of Analysis.—

Known volumes of the standard nickel solution, corresponding to about 0.02 gm. of nickel, were taken for analysis. Larger samples were found difficult to handle owing to the bulky nature of the precipitate. Each sample was diluted with one hundred cubic centimeters of water. The desired salt or acid was then added, followed by ammonia water (28%) until a faint odor of ammonia was perceptible. In some cases an excess of dioxime solution was next slowly added with stirring; in others, preliminary heating to various temperatures was tried. A flocculent red precipitate was always obtained upon introduction of the reagent. When the precipitate showed a tendency to float, vigorous stirring for a few minutes accompanied by cooling caused it to sink to the bottom of the beaker. Then the mixture was filtered using a porous paper. After washing with warm water the paper, with contents, was transferred to a beaker and treated with twenty cubic centimeters of nitric acid (1:1). Warming caused the dioxime to dissolve and the paper to disintegrate. The paper pulp was removed by filtration and the filtrate evaporated after addition of five cubic centimeters of sulfuric acid (95%). Elimination of excess nitric acid and organic matter was thus effected. The residue

was diluted, made ammoniacal and electrolyzed.

At first much trouble was taken to remove traces of organic matter and to secure an electrolyte having the characteristic violet color of an ammoniacal nickel solution. It was discovered however, that this was unnecessary. Solutions varying from dark red through yellow to violet were electrolyzed with no apparent difficulty or difference in results other than a slight increase of the time or current required. The appearance of various colors and the non-interference of the compound producing them led to a modification of the procedure worth mentioning.

The step involving destruction of organic substances by nitric acid followed by evaporation to fumes of  $\text{SO}_3$  for the purpose of removing the excess acid, was replaced by a much quicker process. The dioxime precipitate was dissolved in warm dilute sulfuric acid (1:4) and then ammonium persulfate was added, a few crystals at a time, until the organic matter had been eliminated. The solution, when cooled and diluted, was ready for neutralization. The time required for the operation was approximately fifteen minutes.

(d) Determination of Nickel in the Presence of Iron.

The method described above was used for the analysis of samples containing various amounts of iron, added in the form of a standard solution of ferric sulfate, prepared from very pure electrolytic iron. The concentration of the standard was twenty milligrams of iron per cubic centimeter. Results have been given in Table VI. It is to be noted that ferrous iron, formed by the action of the citrate or tartrate on ferric iron, did not interfere here since the final step was electrolytic in nature.

TABLE VI

Determination of Nickel in Presence of Iron.

| Ni taken<br>gm | Fe taken<br>gm | Added to<br>prevent pptn<br>of Fe | Amount<br>gm | Ni recov.<br>gm | Dif.<br>mgm |
|----------------|----------------|-----------------------------------|--------------|-----------------|-------------|
| .0054          | .50            | Na citrate                        | 4            | .0054           | 0           |
| .0216          | .50            | Na citrate                        | 4            | .0219           | +0.3        |
| .0216          | .50            | Citric acid                       | 4            | .0218           | +0.2        |
| .0216          | .10            | Citric acid                       | 4            | .0216           | 0           |
| .0216          | .20            | Citric acid                       | 4            | .0215           | -0.1        |
| .0108          | .50            | Na tartrate                       | 4            | .0108           | 0           |
| .0217          | .30            | Na tartrate                       | 4            | .0217           | 0           |
| .0217          | .10            | Tartaric acid                     | 4            | .0217           | 0           |
| .0216          | .30            | Tartaric acid                     | 4            | .0217           | +0.1        |

(c) Determination of Nickel in Presence of Manganese, Zinc and Cobalt.

The use of alpha furildioxime for the separation of nickel from manganese, zinc or cobalt offered no advantages over dimethylglyoxime. The method involving precipitation in an acetic acid-sodium acetate solution as recommended by Brunck (56) was not found particularly attractive for removal of nickel from a manganous solution. Zinc was most easily separated in an ammoniacal solution containing ammonium salts. Cobalt solutions were not difficult to handle when the cobalt was in the trivalent ammoniacal form.

### Determination of Nickel in Steel.

Since the analyzed steels obtainable from the Bureau of Standards are representative of those that might be encountered in the industrial world, analyses were made of three different samples:—

|         |                       |                    |
|---------|-----------------------|--------------------|
| No. 32a | a chrome-nickel steel | 1.58% Ni; .89% Cr. |
| No. 33  | a nickel steel        | 3.33% Ni           |
| No. 33a | a nickel steel        | 3.24% Ni           |

The complete analysis of each of these steels as given in the certificate follows:—

TABLE VII

Analyses of Bureau of Standards Steels as given in the Certificates.

|                  | No. 32a | No. 33 | No. 33a |
|------------------|---------|--------|---------|
| Carbon .....     | .396    | .278   | .299    |
| Silicon .....    | .110    | .110   | .124    |
| Phosphorus ..... | .020    | .026   | .027    |
| Sulfur .....     | .017    | .038   | .030    |
| Manganese .....  | .244    | .55    | .456    |
| Nickel .....     | 1.57    | 3.33   | 3.24    |
| Cobalt .....     | —       | .03    | .041    |
| Chromium .....   | .884    | .12    | .197    |
| Copper .....     | .075    | .15    | .080    |
| Arsenic .....    | —       | —      | .012    |
| Tungsten .....   | —       | .15    | —       |
| Molybdenum ..... | —       | .004   | .01     |

#### Details as Regards Nickel

|         | Max.<br>% | Min.<br>% | Avg.<br>% | Method          |
|---------|-----------|-----------|-----------|-----------------|
| No. 32a | 1.59      | 1.52      | 1.56      | Glyoxime        |
|         | 1.63      | 1.57      | 1.59      | "Other Methods" |
| No. 33  | 3.36      | 3.30      | 3.33      | Various         |
| No. 33a | 3.28      | 3.20      | 3.24      | Glyoxime        |
|         | 3.24      | 3.22      | 3.23      | "Other Methods" |



The preparation for precipitation was, in general, the same for all tests. A typical case follows:—

Seven-tenths of a gram of steel was dissolved in fifty cubic centimeters of nitric acid (1:2) and five cubic centimeters of hydrochloric acid (35%). The solution was diluted with two hundred cubic centimeters of water and heated almost to the boiling point. Then six grams of citric acid in about fifteen cubic centimeters of water were added followed by thirty-four cubic centimeters of ammonia water (28%), bringing the total volume up to three hundred cubic centimeters and also giving the proper alkalinity.

These details have been given because, early in the work it was found that success depended upon the presence of the correct amount of ammonium hydroxide, too much exercising a solvent effect on the precipitate while insufficient left the solution acid. In either case the results were low. After a little practice however, it was possible to judge by the color and odor of the solution when conditions were right.

Following precipitation of the nickel furildioxime, various methods were tried for determining the quantity of metal present.

### 1. **Weighing of the Nickel Furildioxime**

(a) In paper (57):—

Samples of steel were dissolved, the nickel precipitated and the precipitates collected on filter papers. These were dried at 120°-130°C and weighed. Subtracting the weight of the filter paper, determined by running a blank, gave the quantity of nickel furildioxime. As a check the precipitates, still wrapped in filter paper were ignited in covered crucibles. Burning took place quietly, without sublimation, at about 300°C. Heating was continued to 750°C. The cooled residues were weighed as Ni O. As a further check, the residues were dissolved in hydrochloric acid, converted to the sulfate and electrolyzed.

The values for the sample given, indicate that the composition of the precipitate at least as regards the nickel is definite and invariable.

TABLE VIII

Analysis of Steel No. 33a by weighing of the nickel furildioxime in paper.

|                          |          |
|--------------------------|----------|
| Ni content .....         | 3.24%    |
| Wt. of sample .....      | .7004 gm |
| Wt. of dioxime.....      | .1943 gm |
| Representing Ni .....    | 3.28%    |
| Wt. of oxide .....       | .0293 gm |
| Representing Ni .....    | 3.27%    |
| Ni by electrolysis ..... | .0227 gm |
| Representing Ni .....    | 3.24%    |

When considering these figures it should be noted that an error of one-tenth milligram in weight of the dioxime would make a difference of only .001% while the same error in either of the other weights would make a difference of .01%. Even so the idea of weighing the dioxime in filter paper without obtaining the weight of the particular piece of paper involved cannot be recommended for accurate work. In one package of paper used for this investigation variations in weight of as much as 0.026 gm were found.

(b) In a Gooch.—

The same method as given above was followed except that gooch crucibles with asbestos mats were used in place of the filter paper. This was attended with a certain difficulty, viz:—the precipitate tended to form a dense layer at the bottom of the crucible and retard filtration. The impediment was partially avoided by using mild suction—seventy to eighty millimeters of mercury—and washing by decantation.

There is one important point to be noted in connection with the procedure under consideration. As stated in the section dealing with qualitative tests ferrous iron gives a purple precipitate with alpha-furildioxime. It has long been known that organic compounds such as citrate and tartrate reduce ferric to ferrous iron especially in the sunlight. (58) Hence if compounds of either of these radicals are used to prevent the precipitation of iron when the solution is made ammoniacal, there is danger of contamination of the nickel furildioxime.

When considering this difficulty a relation was noted between the time intervening between precipitation and filtration, and the amount of contamination. To secure quantitative data the iron in some of the impure precipitates was determined. Assuming that it had existed in the dioxime precipitate as ferrous furildioxime,  $\text{Fe}(\text{C}_{10}\text{H}_7\text{N}_2\text{O}_4)_2$  the weight of iron found was calculated to that compound and subtracted

from the weight of impure dioxime. Converting the corrected weight to its nickel equivalent gave results checking well with the known nickel content of the original sample. Data for this work have been assembled in Table IX.

TABLE IX

Showing contamination of nickel furildioxime by ferrous furildioxime (?) when nickel was precipitated from a solution in which the precipitation of ferric iron was prevented by use of citrate or tartrate.

Steel No. 33a containing 3.24% nickel

| Sample<br>gm | Impure<br>ppt. gm | Ni value<br>% | Fe <sub>2</sub> O <sub>3</sub><br>gm | Corrected<br>wt. of diox-<br>ime gm | Ni found<br>% | Filt. after<br>pptn. hrs. |
|--------------|-------------------|---------------|--------------------------------------|-------------------------------------|---------------|---------------------------|
| .7004        | .1943             | 3.28          | no ppt.                              | —                                   | 3.28          | .5                        |
| .7025        | .2076             | 3.49          | .0021                                | .1946                               | 3.27          | 1.0                       |
| .7004        | .2106             | 3.55          | —                                    | —                                   | —             | 2.0                       |
| .7009        | .2160             | 3.64          | .0032                                | .1962                               | 3.30          | 3.0                       |

(The first sample contained tartaric, the others citric acid.)

It will be seen from these figures that the error becomes negligible if the solution is filtered in less than one-half hour after precipitation. Of course the difficulty can be entirely eliminated by use of sodium pyrophosphate, possibly also by working in artificial light.

## 2. Precipitation as Nickel Furildioxime followed by ignition to NiO.—

Brunck (59) noted that nickel dimethylglyoxime sublimes when heated to 250°C. To determine whether nickel furildioxime would do the same, samples were slowly heated in an electric muffle under varying conditions. No sublimation was observed. It was found, however, that the dioxime if contained in an open Gooch crucible would ignite suddenly with a slight explosion at about 250°C., thus endangering the expulsion of some of the precipitate by the gases so rapidly evolved. When the precipitates were contained in filter paper and placed in a covered porcelain crucible, ignition took place quietly at about 300°C with no sudden release of gases. The covers were then removed and the temperature rapidly raised to 750°C. After cooling, the nickel was weighed. The results were entirely satisfactory as is shown by the analysis given on page 23 as well as the following :—

TABLE X

Ignition of Nickel furildioxime to NiO

Steel No. 33a containing Ni 3.24%

|                          |          |       |
|--------------------------|----------|-------|
| Wt. of sample .....      | .7004 gm |       |
| Wt. of NiO .....         | .0291 gm |       |
| Representing Ni .....    |          | 3.26% |
| Ni by electrolysis*..... | .0229 gm |       |
| Representing Ni .....    |          | 3.27% |

(\* The NiO was dissolved, converted to the sulfate and electrolyzed.)

Note:—The analyses cited were made at night using tartaric acid to prevent precipitation of ferric iron. Filtration took place one-half hour after precipitation.

### 3. Cyanide Titration after Separation as Nickel Furildioxime.

The nickel was precipitated from a weighed sample as usual, separated by use of a porous filter paper and transferred to a beaker. Addition of fifteen cubic centimeters of concentrated nitric acid, followed by heating, quickly dissolved the precipitate and destroyed the major portion of the organic matter. The solution was diluted with twenty cubic centimeters of water and filtered to remove the paper pulp. A few crystals of ammonium persulfate were added to the filtrate which was then heated to insure destruction of traces of organic matter. The subsequent steps were according to the procedure described by Campbell and Andrews (60) for the determination of nickel by cyanide titration. The results have been gathered in Table XI for four consecutive samples. The total time spent on these four samples was less than two hours.

TABLE XI

Nickel determined by separation as nickel furildioxime followed by cyanide titration.

Steel No. 33 containing Ni 3.33%

| Wt. Sample | KCN   | Ni found |
|------------|-------|----------|
| gm         | cc.   | %        |
| .7201      | 25.20 | 3.33     |
| .7096      | 24.70 | 3.32     |
| .7720      | 27.00 | 3.34     |
| .8289      | 28.80 | 3.32     |

The standard cyanide solution was made up as suggested by Campbell and Andrews (60) except that one gram of potassium hydroxide was added to prevent hydrolysis. The nickel value was obtained by standardization against the standard nickel solution.



TABLE XII

## Standardization of Potassium Cyanide Solution.

| Std. Ni. taken | KCN required | Ni value            |
|----------------|--------------|---------------------|
| cc.            | cc.          | gm. per cc.         |
| 20.02          | 22.55        | .00095              |
| 20.13          | 23.08        | .00094              |
| 20.26          | 22.65        | .00096              |
|                |              | Average..... .00095 |

4. **Electrolysis.**—

Electrolytic determinations by the procedure already given (~~p 17~~) were made using steels No. 33a and No. 32a. The results are given in Table XIII.

TABLE XIII

## Separation of Nickel in Steel as nickel furildioxime; determination as metallic nickel by electrolysis.

| Steel No. | Ni content % | Wt. sample gm | Wt. deposit gm | Ni found % |
|-----------|--------------|---------------|----------------|------------|
| 33a       | 3.24         | .7559         | .0247          | 3.26       |
|           |              | .8007         | .0259          | 3.23       |
| 32a       | 1.58         | 1.0033        | .0157          | 1.56       |
|           |              | 1.0560        | .0167          | 1.58       |
|           |              | 1.0313        | .0162          | 1.57       |

**Summary**

1. Alpha furildioxime may be used to detect nickel 1:6,000,000.
2. Alpha furildioxime may be used for the quantitative separation and determination of nickel, especially in steel.
3. Alpha furildioxime is sufficiently soluble in hot water to make possible the use of an aqueous solution if desired.
4. Alpha furildioxime in solution is a stable reagent. Samples made up in both water and alcohol have been kept for five months with no apparent decomposition or change in precipitating power.
5. Nickel furildioxime is readily soluble in nitric or dilute sulfuric acid.
6. After separation the determination may be made by direct weighing of the dioxime, by ignition to NiO, by cyanide titration or by electrolysis.
7. When preparing a solution for electrolysis last traces of the organic matter do not need to be destroyed.
8. Ferrous iron gives a precipitate with alpha furildioxime. This precipitate probably is ferrous furildioxime,  $\text{Fe}(\text{C}_{10}\text{H}_7\text{N}_2\text{O}_4)_2$ .

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